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(54) Clathrate compounds and processes for production thereof

(57) Group IV metal clathrate compounds comprising, as the structural unit of crystals, Me_{46} clusters (Me is Si or Ge) with each consisting of Me_{20} and Me_{24} clusters having cage structures, where the Me_{20} cluster encapsulate alkali metal (A) atoms and the Me_{24} cluster encapsulates alkaline earth metal (Ae) atoms, and has a composition represented by the following formula:



wherein

A is Li_4 , Na, K, Rb or Cs;

Ae is Ba, Sr or Ca;

Me is Si or Ge;

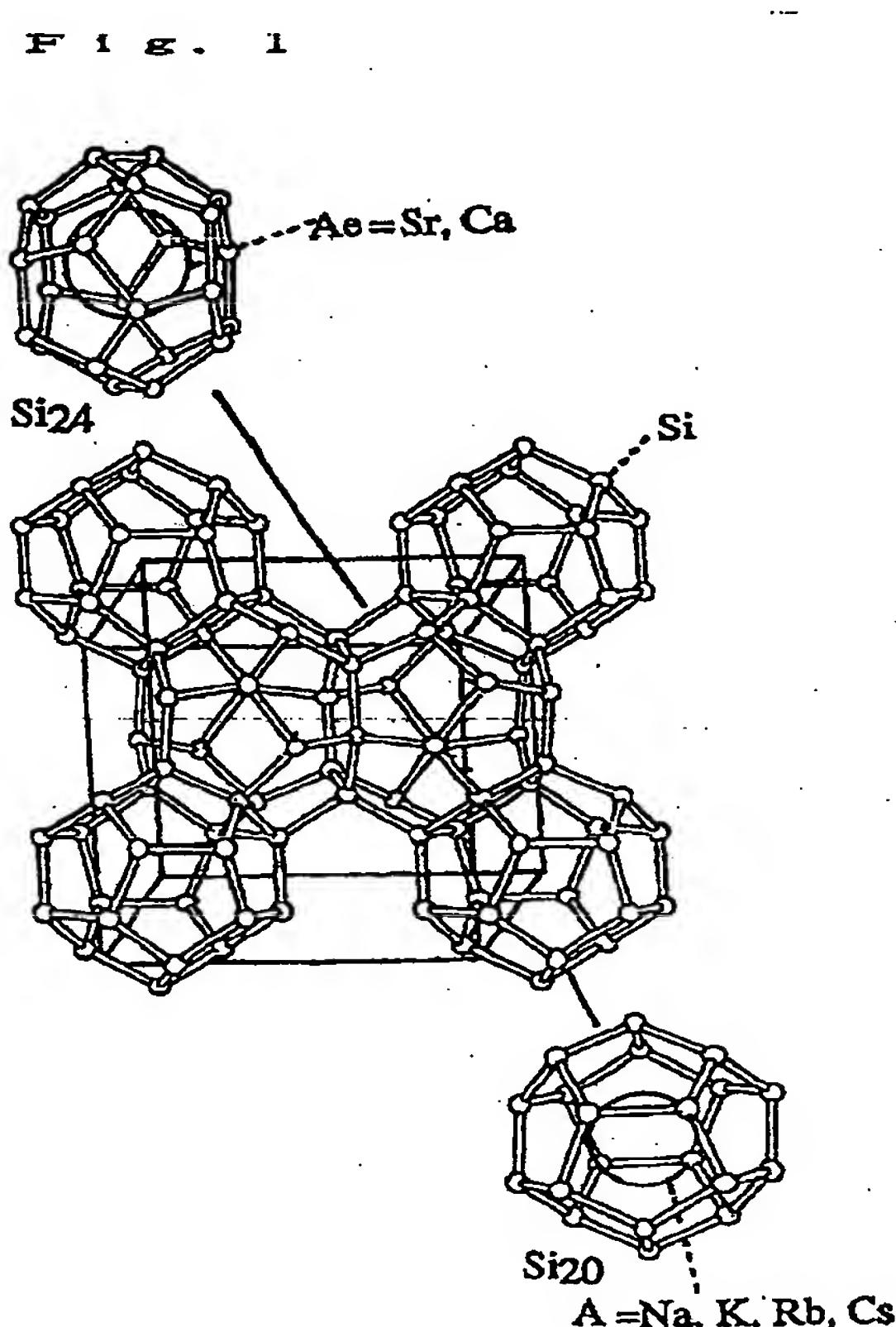
x is the number ratio of A relative to the other elements and is 0 to 2;

when Me is Si and A is Na, K, Rb or Cs, Ae is Sr or Ca;

when Me is Si and A is Li_4 , Ae is Ba, Sr or Ca; and

when Me is Ge, A is Na, K, Rb or Cs and Ae is Ba, Sr or Ca.

These clathrate compounds can show the properties ranging from an insulator, a semiconductor, a conductor to a superconductor, by appropriately selecting the type of Ae as well as A.



Other object of the present invention is to provide novel electronic materials with different electrical properties, by encapsulating appropriately selected metals inside the cluster cage of the above clathrate compounds.

The silicon or germanium clathrate compounds of the present invention capable of achieving the above objects include the followings:

a silicon clathrate compound of the following composition:



[wherein A is an alkali metal element selected from the group consisting of Na, K, Rb and Cs; Ae is an alkaline earth metal element selected from the group consisting of Sr and Ca; and x is the number ratio of the alkali metal element to other elements and $0 \leq x \leq 2$], which comprises, as a structural unit of crystals, Si_{46} cluster with each consisting of Si_{20} clusters and Si_{24} clusters having cage structures formed by silicon atoms of the framework of the crystal,

at least a part of said Si_{24} clusters encapsulating alkaline earth metal atoms inside the cage, and optionally at least a part of Si_{20} clusters encapsulating alkali metal atoms inside the cage;

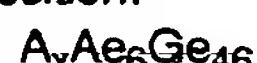
a silicon clathrate compound of the following composition:



[wherein Ae is an alkaline earth metal element selected from the group consisting of Ba, Sr and Ca], which comprises, as a structural unit of crystals, Si_{46} cluster with each consisting of Si_{20} clusters and Si_{24} clusters having cage structures formed by silicon atoms of the framework of the crystal,

at least a part of said Si_{24} clusters encapsulating alkaline earth metal atoms inside the cage, and at least a part of Si_{20} clusters encapsulating clustered Li_4 par Si_{20} cluster;

a germanium clathrate compound of the following composition:



[wherein A is an alkali metal element selected from the group consisting of Na, K, Rb and Cs; Ae is an alkaline earth metal element selected from the group consisting of Ba, Sr and Ca; and x is the number ratio of the alkali metal element to other elements and $0 \leq x \leq 2$], which comprises, as a structural unit of crystals, Ge_{46} cluster with each consisting of Ge_{20} clusters and Ge_{24} clusters having cage structural formed by germanium atoms of the framework of the crystal,

at least a part of said Ge_{24} clusters encapsulating alkaline earth metal atoms inside the cage, and optionally at least a part of Ge_{20} clusters encapsulating alkali metal atoms inside the cage, so as to provide said composition;

Each of the silicon or germanium clathrate compounds of the present invention has no crystal structure of the conventional sp^3 bond but has a crystal structure of the particular bond which is intermediate between sp^3 bond and sp^2 bond, because it has, as the minimum structural units of crystals, clusters with each having 20 silicon or germanium atoms and clusters with each having 24 silicon or germanium atoms.

The silicon clathrate compound $A_xAe_6Si_{46}$ of the present invention differs from the conventional silicon clathrate compound encapsulating a Ba atom in each Si_{24} cluster unit, because the present compound encapsulates an alkaline earth metal atom other than Ba in each Si_{24} cluster unit.

The present silicon clathrate compound $(Li_4)_2Ae_6Si_{46}$ encapsulating a lithium cluster consisting of four lithium atoms in each Si_{20} cluster unit and encapsulating an alkaline earth metal atom in each Si_{24} cluster unit, is different from the conventional silicon clathrate compound, because the present compound encapsulates a lithium cluster in each Si_{20} cluster unit.

The present germanium clathrate compound $A_xAe_6Ge_{46}$ having germanium as the framework of the crystal and is different from the conventional silicon clathrate compound.

In the conventional techniques, it was thought that Ba is the only alkaline earth metal that can be encapsulated in the Si_{24} clusters of silicon clathrate compound. In fact, there is no report of any kind concerning the successful synthesis of a silicon clathrate compound encapsulating an alkaline earth metal (e.g. Sr or Ca) other than Ba, also in the experimental level.

With respect to germanium clathrate compounds, no attempt has been made on the synthesis of any Ba-encapsulating clathrate compounds and, of course, no success has been reported.

Thus, as the clathrate compound which has the bonding mode above and can actually be synthesized, only known has been $A_xBa_6Si_{46}$ using Si as the framework element.

In the conventional techniques, only a silicon clathrate compound encapsulating Ba as an alkaline earth metal was synthesized. The reason is thought to be as follows.

$A_2Ba_6Si_{46}$ (A is Na or K) his been synthesized by a conventional process by preparing a ASi-BaSi₂ solid solution (e.g. A_2BaSi_4) having Si_4 clusters as the basic structure, from two types of starting materials, ASi and BaSi, being followed by an alkali-removing treatment of the solid solution with heating in vacuum to change the crystal structure into the clathrate [S. Yamanaka et al., Fullerene Science & Technology, 3 (1), 21-28 (1995)].

The reason why, in the above, only Ba was encapsulated as an alkaline earth metal and neither Sr nor Ca was investigated, is that only BaSi₂, similarly to ASi, has a cubic crystal structure containing tetrahedral Si_4 clusters with each having the cage structure of four silicon atoms and thus a solid solution (a precursor to the clathrate compound) having Si_4 clusters as the important

DETAILED DESCRIPTION OF THE INVENTION AND PREFERRED EMBODIMENTS

The Group IV metal clathrate compounds of the present invention have a basic crystal structure composed of Me_{46} clusters (Me is Si or Ge) each consisting of (1) Me_{20} clusters of a dodecahedral cage of 20 silicon or germanium atoms and (2) Me_{24} clusters with each having a tetradecahedral cage of 24 silicon or germanium atoms.

The first embodiment of the silicon clathrate compounds of the present invention has, as mentioned previously, the composition represented by the following formula:



wherein A is Na, K, Rb or Cs; Ae is Sr or Ca; and x is a real number of 0 to 2 and indicates the atom number ratio of A to other elements.

When the above compound contains an alkali metal (A), the alkali metal atom is encapsulated in part or all of the Si_{20} clusters.

Therefore, the silicon clathrate compound of the first embodiment has the following three cases.

- I. No alkali metal atom is encapsulated in any Si_{20} cluster.
- II. There are two kinds of Si_{20} clusters, one kind of Si_{20} cluster(s) with each encapsulating alkali metal atoms and the other one(s) with each encapsulating no alkali metal atom.
- III. Each of the Si_{20} clusters encapsulates alkali metal atom(s).

Incidentally, when the alkali metal is Li, part or all of the Si_{20} clusters can encapsulate a cluster composed of more than one Li atom, for example, a cluster composed of 4 Li atoms. When the alkali metal is other than Li, one alkali metal atom is generally encapsulated in one Si_{20} cluster.

This is presumed to be because a Li atom has a significantly small ionic radius (0.78 Å) as compared with those of other alkali metal atoms and each Si_{20} cluster can provide an enough space for encapsulating some members of Li atoms. Li_4 is the most stable cluster in Li.

Hence, the second embodiment of the silicon clathrate compounds of the present invention has, as mentioned previously, the composition represented by the following formula:



wherein Ae is Ba, Sr or Ca.

The germanium clathrate compound of the present invention has, as mentioned previously, the composition represented by the following formula:



wherein A is an alkali metal; Ae is Ba, Sr or Ca; and x is a real number of 0 to 2 and indicates the atom number ratio of A to the other elements. This germanium clathrate compound, similarly to the silicon clathrate compound of the first embodiment, has the following cases.

- I. No alkali metal atom is encapsulated in any Ge_{20} cluster.
- II. There are two kinds of Ge_{20} clusters; one kind of Ge_{20} cluster(s) with each encapsulating an alkali metal atom(s) and the other one(s) with each encapsulating no alkali metal atom.
- III. Each of the Ge_{20} clusters encapsulates alkali metal atom(s).

In the above-mentioned clathrate compounds of the present invention, the alkaline earth metal is encapsulated in the Me_{24} clusters (Me is Si or Ge).

The clathrate compounds of the present invention can be produced, for example, by the following processes.

A. Processes for production of silicon clathrate compounds

First, an alkali metal (A) and Si are mixed, and the mixture is placed in a PBN or a tungsten container. The tube is sealed in a stainless steel tube and heated under inert gas atmosphere like Ar at 500-650°C to obtain an ASi compound. The heating can preferably be conducted by the use of, for example, an electric furnace.

Next, an alkaline earth metal (Ae) and Si are mixed, and the mixture is heated to about 900-1,200°C in an atmosphere of an inert gas, for example, argon to synthesize an AeSi₂ compound. The heating can preferably be conducted by the use of, for example, high-frequency induction heating.

The above-obtained ASi compound and AeSi₂ compound are mixed at a stoichiometric ratio of 2:1 and heated at about 600°C to synthesize a ternary solid solution A₂AeSi₄.

Finally, the ternary solid solution is heat-treated by controlling pressure with an inert gas under vacuum (20-200 Torr) in a heating furnace whose temperature can be controlled to 300-600°C very accurately, and is then subjected to distillation of alkali metals, whereby a desired silicon clathrate compound can be formed.

Resulting products during the reaction can be easily removed from the above-obtained product, because BaSi₂, etc. produced as by-products are water-soluble and easily removable by a treatment with an acidic aqueous solution, and a desired silicon clathrate compound can be isolated in a pure form.

The number ratio (x) of the alkali metal can be controlled by selecting an appropriate conditions.

The alkali metal can be Na, K, Rb or Cs; and the

present invention, unlike conventional Ge crystals, can have a variety of properties ranging from insulator, semiconductors with different band gaps, metal to superconductor, by appropriately selecting the type and the amount of the alkaline earth metal encapsulated. This suggests a possibility that a semiconductor device with high performance can be produced using germanium, alkali metals and alkaline earth metals, all of which exist in rich natural abundance on the earth and pose little public hazard and pollution problem.

Further, the germanium clathrate compounds of the present invention, having a band with narrow dispersion, show a large property change against external influences; that is, they can exhibit a sensing function not possessed in conventional clathrate compounds reported as far and larger giant magneto resistance than in conventional materials.

The present invention is hereinafter described in more detail by way of Examples.

Example 1

A 1:1 mixture of Na (230 mg) and Si (281 mg) was placed in a PBN container. The PBN was sealed in a stainless steel tube in an argon atmosphere and heated at 650°C for 5 hours to give rise to a reaction. The reaction system was cooled down to room temperature and the reaction product (NaSi) was taken out. The crystal form of the compound was examined by X-ray analyses, which showed a monoclinic crystal system (space group: C2/C).

A 1:2 mixture of Sr (440 mg) and Si (281 mg) was heated in an argon atmosphere by high-frequency induction heating at 30A (temperature: about 1,200°C) for 10 minutes to give rise to a reaction. The reaction system was cooled down to room temperature, and the reaction product (SrSi₂) was yielded. The crystal form of the compound was examined by X-ray analysis, which showed a cubic crystal system (space group: 32P4₃).

The above-obtained two compounds, NaSi and SrSi₂, were mixed at a molar ratio of 2:1 and placed in a PBN container. The PBN was sealed in a stainless steel tube in an argon atmosphere and heated at 650°C for 48 hours to give rise to a reaction. The reaction system was cooled to room temperature and the reaction product was taken out. The product was a uniform solid solution with a composition of Na₂SrSi₄, having a crystal structure similar to that of NaSi, i.e. Si₄ clusters exist as the basic structural unit of crystals.

The solid solution was heated at 400°C for 150 hours under vacuum of 20 Torr, whereby an intended clathrate compound with a composition of Na₂Sr₆Si₄₆ was synthesized.

The reaction system was cooled to room temperature; and the reaction product was taken out, washed with 0.1 N hydrochloric acid and water in this order, and dried to obtain a purified product. The purified product was subjected to elemental analysis, which indicated Na_{1.8}Sr_{6.1}Si₄₆.

5 The purified product was also subjected to X-ray analysis, which confirmed that the product was a clathrate compound showing an intended crystal structure. The properties of the compound were measured and found to be metallic and superconducting with a critical temperature of 4K.

Example 2

10 A 1:1 mixture of K (696 mg) and Si (500 mg) was placed in a PBN container. The PBN was sealed in a stainless steel tube in an argon atmosphere and heated at 650°C for 5 hours to give rise to a reaction. The reaction system was cooled to room temperature and the reaction product (KSi) was taken out. The crystal form 15 of the compound was examined by X-ray analysis, which showed a cubic crystal system [space group: P-4 (axis of four rotary inversions) 3n].

20 The above-obtained KSi compound and the SrSi₂ synthesized in Example 1 were mixed at a molar ratio of 2:1 and placed in a PBN cell. The PBN was sealed in a stainless steel tube in an argon atmosphere and heated at 650°C for 48 hours to give rise to a reaction. The reaction system was cooled to room temperature and the reaction product was taken out. The product was a uniform solid solution with a composition of K₂SrSi₄, having a crystal structure similar to those of NaSi and KSi.

25 The solid solution was heated at 370°C for 120 hours under vacuum of 50 Torr, whereby an intended clathrate compound having a composition of K₂Sr₆Si₄₆ was synthesized.

30 The reaction system was cooled down to room temperature; and the reaction product was taken out, washed with 0.1 N hydrochloric acid and water in this order, and dried to obtain a purified product. The purified product was subjected to elemental analysis, which indicated K_{1.9}Sr_{6.2}Si₄₆.

35 The purified product was also subjected to X-ray analysis, which confirmed that the product was a clathrate compound having an intended crystal structure. The properties of the compound were measured and found to be metallic and superconducting with a critical temperature of 3.5K.

Example 3

40 A 1:2 mixture of Ca (201 mg) and Si (281 mg) was heated in an argon atmosphere by high-frequency induction heating at 30A (temperature: about 1,200°C) for 10 minutes to give rise to a reaction. The reaction system was cooled to room temperature, and the reaction product (CaSi₂) was taken out. The crystal structure 45 of the compound was examined by X-ray analysis, which showed a trigonal crystal system [space group: R-3 (axis of three rotary inversions) m].

50 The above-obtained CaSi₂ compound and the NaSi synthesized in Example 1 were mixed at a molar ratio of 1:2 and placed in a PBN cell. The PBN was sealed in a

placed in a PBN cell. The PBN was sealed in a stainless steel tube in an argon atmosphere and heated at 650°C for 48 hours to give rise to a reaction. The reaction system was cooled to room temperature and the reaction product was taken out. The product was a uniform solid solution with a composition of K_2BaGe_4 , showing a crystal structure similar to that of KGe.

The solid solution was heated at 370°C for 200 hours under vacuum of 50 Torr, whereby an intended clathrate compound having a composition of $K_2Ba_6Ge_{46}$ was synthesized.

The reaction system was cooled to room temperature; and the reaction product was taken out, washed with 0.1 N hydrochloric acid and water in this order, and dried to obtain a purified product. The purified product was subjected to elemental analysis, which indicated $K_{1.9}Ba_{6.2}Ge_{46}$. The purified product was also subjected to X-ray analysis, which confirmed that the product was a germanium clathrate compound having an intended crystal structure. The properties of the compound were measured and found to be a metal with an electrical conductivity of 500 Scm^{-1} .

Example 7

A 1:2 mixture of Ca (400 mg) and Ge (1,452 mg) was heated in an argon atmosphere by high-frequency induction heating at 30A (temperature: about 1,200°C, for 10 minutes to give rise to a reaction. The reaction system was cooled to room temperature, and the reaction product ($CaGe_2$) was taken out. The crystal form of the compound was examined by X-ray analysis, which showed a crystal of space group = hR6.

The above-obtained $CaGe_2$ and the NaGe obtained in Example 5 were mixed at a molar ratio of 1:2 and placed in a PBN cell. The PBN was sealed in a stainless steel tube in an argon atmosphere and heated at 650°C for 48 hours to give rise to a reaction. The reaction system was cooled to room temperature and the reaction product was taken out. The product was a uniform solid solution with a composition of Na_2CaGe_4 , having a crystal structure similar to that of NaGe (except for the expanded lattice) but greatly different from that of $CaGe_2$.

The solid solution was heated at 400°C for 150 hours under vacuum of 50 Torr, whereby an intended clathrate compound with a composition of $Na_2Ca_6Ge_{46}$ was synthesized.

The reaction system was cooled down to room temperature, and the reaction product was taken out, washed with 0.1 N hydrochloric acid and water in this order, and dried to obtain a purified product. The purified product was subjected to elemental analysis, which indicated $Na_{1.9}Ca_{6.1}Ge_{46}$. The purified product was also subjected to X-ray analysis, which confirmed that the product was a germanium clathrate compound having an intended crystal structure. The compound was measured for electrical conductivity, which showed that it is a semiconductor with a relatively small band gap

(about 0.2 eV).

Example 8

5 A 1:2 mixture of Sr (876 mg) and Ge (1,450 mg) was heated in an argon atmosphere with a high-frequency induction method at 30A (temperature: about 1,200°C) for 10 minutes hours to give rise to a reaction. The reaction system was cooled to room temperature, 10 and the reaction product ($SrGe_2$) was taken out. The crystal form of the compound was examined by X-ray analysis, which showed a crystal of space group = oP12.

The above-obtained $SrGe_2$ and the NaGe obtained 15 in Example 5 were mixed at a molar ratio of 1:2 and placed in a PBN cell. The PBN was sealed in a stainless steel tube in an argon atmosphere and heated at 650°C for 48 hours to give rise to a reaction. The reaction system was cooled to room temperature and the reaction 20 product was taken out. The product was a uniform solid solution with a composition of Na_2SrGe_4 , having a crystal structure similar to that of NaGe (except for the expanded lattice) but different from that of $SrGe_2$.

The solid solution was heated at 420°C for 150 25 hours under vacuum of 50 Torr, whereby an intended clathrate compound having a composition of $Na_2Sr_6Ge_{46}$ was synthesized.

The reaction system was cooled to room temperature; and the reaction product was taken out, washed 30 with 0.1 N hydrochloric acid and water in this order, and dried to obtain a purified product. The purified product was subjected to elemental analysis, which indicated $Na_{1.5}Sr_{6.3}Ge_{46}$. The purified product was also subjected to X-ray analysis, which confirmed that the product 35 was a germanium clathrate compound having an intended crystal structure. The properties of the compound were measured and found to be a semi-conductor with a relatively small band gap (about 0.1 eV).

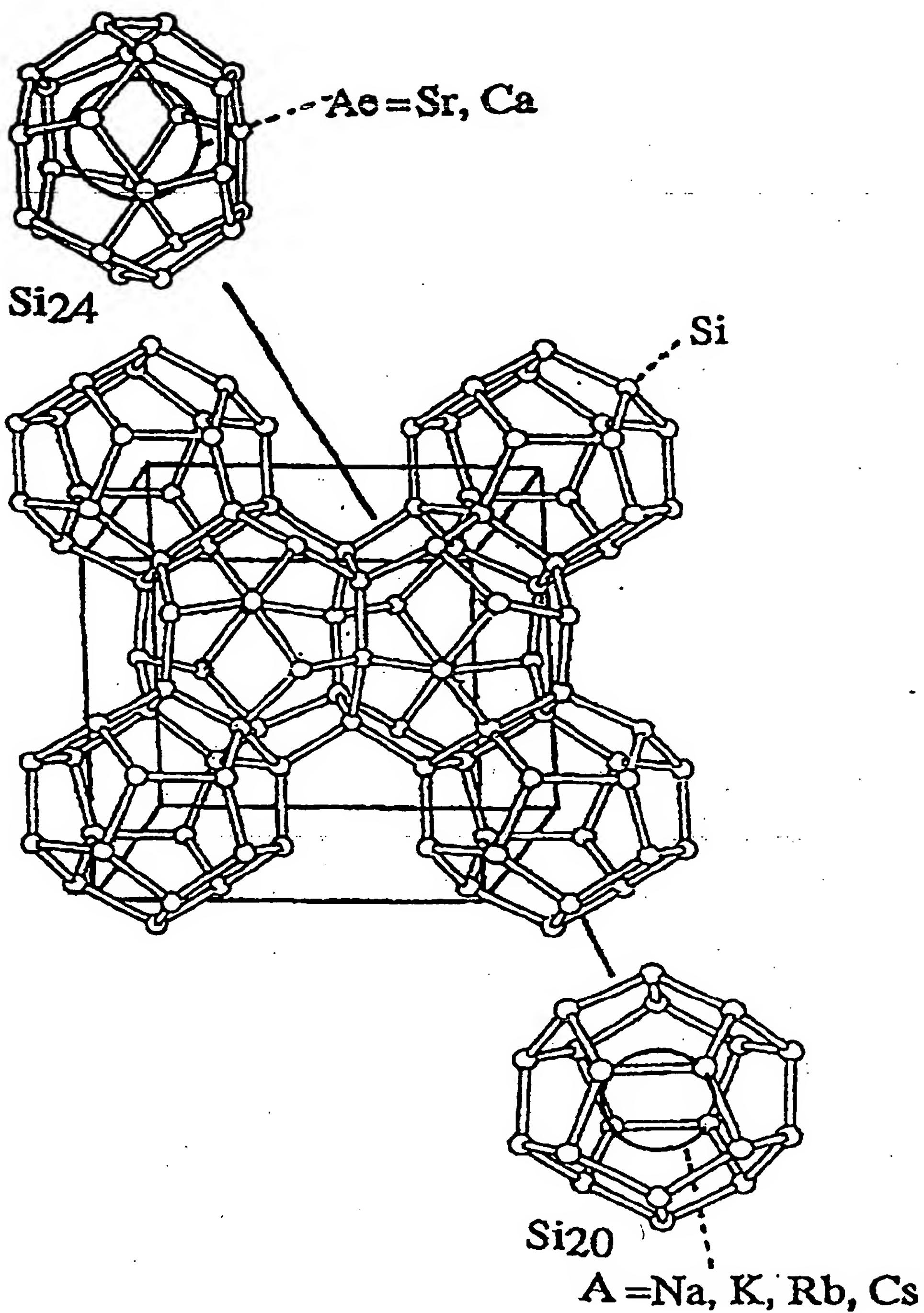
Claims

1. A silicon clathrate compound of the following composition:

$A_xAe_6Si_{46}$
[wherein A is an alkali metal element selected from the group consisting of Na, K, Rb and Cs; Ae is an alkaline earth metal element selected from the group consisting of Sr and Ca; and x is the number ratio of the alkali metal element to the other elements and $0 \leq x \leq 2$], which comprises, as the structural unit of crystals, Si_{46} clusters, each of which consists of Si_{20} clusters and Si_{24} clusters with cage structures formed by silicon atoms as the framework of the crystal,

55 at least a part of said Si_{24} clusters encapsulating alkaline earth metal atoms inside the cage, and optionally at least a part of Si_{20} clusters encapsulating alkali metal atoms inside the cage.

F i g . 1





EUROPEAN SEARCH REPORT

Application Number
EP 96 12 0943

DOCUMENTS CONSIDERED TO BE RELEVANT									
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)						
D,A	FULLERENE SCIENCE & TECHNOLOGY, vol. 3, no. 1, 1995, NEW YORK, US, pages 21-28, XP000645540 S. YAMANAKA ET AL.: "Preparation of barium-containing silicon clathrate compound" * page 26, line 4 - line 10; page 27 : figure 2 * ---	1	C01B33/06 C22C28/00 //H01L39/12, H01L29/24, H01B1/06						
A	PHYSICAL REVIEW LETTERS, 20 FEB. 1995, USA, vol. 74, no. 8, ISSN 0031-9007, pages 1427-1429, XP000646872 KAWAJI H ET AL: "Superconductivity in the silicon clathrate compound (Na,Ba)/sub x/Si/sub 46/" * abstract; page 1428 : figure 2 and right-hand column, paragraph 2 * ---	1							
A	EUROPEAN JOURNAL OF SOLID STATE AND INORGANIC CHEMISTRY, 1995, FRANCE, vol. 32, no. 7-8, ISSN 0992-4361, pages 799-807, XP000646873 YAMANAKA S ET AL: "Preparation and superconductivity of barium containing silicon clathrate compound, (Ba,K)/sub x/Si/sub 46/" * abstract; page 804 : figure 3 and line 2 - line 6 * -----	1	TECHNICAL FIELDS SEARCHED (Int.Cl.6) C01B C22C						
<p>The present search report has been drawn up for all claims</p> <table border="1"> <tr> <td>Place of search</td> <td>Date of completion of the search</td> <td>Examiner</td> </tr> <tr> <td>THE HAGUE</td> <td>7 April 1997</td> <td>Brebion, J</td> </tr> </table> <p>CATEGORY OF CITED DOCUMENTS</p> <p>X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document</p> <p>T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document</p>				Place of search	Date of completion of the search	Examiner	THE HAGUE	7 April 1997	Brebion, J
Place of search	Date of completion of the search	Examiner							
THE HAGUE	7 April 1997	Brebion, J							